^{121}Sb MÖSSBAUER SPECTRA OF ANTIMONY OXIDES

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^{121}Sb Mössbauer spectra have now been reported (1-4) for a sufficient

number of antimony compounds to conclude that, relative to a ^{121}SnO$_2$(Sb) source,

inorganic antimony(III) compounds have isomer shifts (I.S.) more negative than

-11 mm/sec and inorganic antimony(V) compounds have isomer shifts between

-4 and +4 mm/sec. The isomer shifts reported for Sb$_2$O$_3$ (4), cubic Sb$_2$O$_3$ (sen-

armentite) (1) and Sb$_2$O$_5$ (2,4) are consistent with the oxidation numbers

usually assigned to the antimony in these compounds (See Table I.). There is

a third antimony oxide, Sb$_2$O$_4$, the Mössbauer spectrum of which should be of

considerable interest since the antimony could be either Sb(IV) or consist of

equal numbers of Sb(III) and Sb(V). X-ray results, which show that α-Sb$_2$O$_4$

(cervantite) (5) is isostructural with Sb^{III}Nb^{V}O$_4$ and Sb^{III}Ta^{V}O$_4$ and that

β-Sb$_2$O$_4$ consists of equal numbers of 4- and 6-coordinate antimony atoms, have

led to the conclusion that both polymorphs contain Sb(III) and Sb(V) rather

than Sb(IV) (6). We have determined the ^{121}Sb Mössbauer spectrum of cervantite

to verify these conclusions, redetermined the Mössbauer spectra of senarmentite

and of Sb$_2$O$_5$ so that comparisons can be made with spectra determined on the

same equipment and source, and determined the spectra of amorphous Sb$_2$O$_3$ and

of orthorhombic Sb$_2$O$_3$ (valentinite) to complete the series of oxides.

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ANTIMONY OXIDES

TABLE I

Summary of Reported Antimony Oxide Mössbauer Parameters

Compound	Sample Temp., °K	Reported IS (mm/sec)	Reference Material	IS Relative to $^{121}SnO_2$(Sb) (mm/sec)	QS (mm/sec)
Cubic Sb_2O_3 [a]	4.2	-0.56 ± 0.02	β-Sn(Sb)	-11.37 ± 0.2 [d]	18.72 ± 0.40
Sb_2O_3 [b]	4.2	-3.02 ± 0.05	InSb	-11.17 ± 0.1 [d]	18.8 ± 0.40
Sb_2O_3 [c]	~78	-10.4 ± 0.3	SnO_2(Sb)	-10.4 ± 0.3	
Sb_2O_5 [c]	~78	0.0 ± 0.2	SnO_2(Sb)	0.0 ± 0.2	
Sb_2O_5 [b]	4.2	9.9 ± 0.2	InSb	1.6 ± 0.3	-8.4 ± 0.8

[a] Reference 1.
[b] Reference 2.
[c] Reference 4.
[d] Converted by using -8.15 ± 0.06 mm/sec as the isomer shift for InSb (at 78°K) with respect to a $^{121}SnO_2$(Sb) source and -2.66 ± 0.1 mm/sec for the conversion between β-Sn(Sb) and SnO_2(Sb) sources (2).

Experimental

Materials. Reagent grade antimony trioxide was purchased from J. T. Baker Chemical Co., and on the basis of an x-ray powder diffraction pattern, this material was estimated to consist of 10% orthorhombic Sb_2O_3 and 90% cubic Sb_2O_3. Portions of this material were converted to pure phases as follows: *cubic*—a sample of the above Sb_2O_3 was heated in an evacuated Vycor tube at 520° for 12 hours and then allowed to cool to room temperature (7); *ortho-rhombic*—a sample of the reagent grade Sb_2O_3 was melted under a helium atmosphere in a Vycor tube and then the melt was quenched by pouring it onto a refractory tile at room temperature (8); *amorphous Sb_2O_3*—a sample of the reagent grade Sb_2O_3 was heated at 600° for 15 hours in a quartz tube and then allowed to cool at room temperature. An x-ray powder diffraction pattern was determined for each of the preparations and was found to conform to those

published in the literature (8,9). The amorphous sample of course showed no
diffraction lines. α-Sb_2O_4, cervantite, was obtained from Rocky Mountain
Research, Inc., Denver, Colorado as 99.999% "Antimony(IV) Oxide"; 99.5% anti-
mony pentoxide was purchased from Research Organic/Inorganic Chemical Co.,
Sun Valley, Calif. X-ray powder patterns also were determined for these
materials, and they were found to have only lines characteristic of these
respective oxides (8).

Spectra. The Mössbauer spectrometer consisted of an Austin Science Asso-
ciates S-3 constant acceleration drive unit, a xenon-methane proportional
counter, a Nuclear Data 512 channel analyzer, a single channel analyzer set on
the escape peak of the 37 kev ^{121}Sb gamma and a ~150 μc $^{121}SnO_2$(Sb) source.
The velocity scale was calibrated with a Pd(^{57}Co) source and a metallic iron
foil. The antimony spectra were determined with both source and absorbers
maintained at liquid nitrogen temperature. Absorbers were prepared by dilut-
ing the powdered sample with powdered polyethylene and placing this mixture
in Lucite holders in such a manner as to obtain a sample thickness of ~12 mg
Sb/cm^2 (24 mg Sb/cm^2 was used in the case of α-Sb_2O_4). The spectra were fit-
ted by a computer program to an eight-line quadrupole pattern (the ratio of
the quadrupole moment of the excited state to ground state was taken as 1.32).
In each case the best fit was deemed reasonable on the basis of the Chi-square
value.

Results and Discussion

All of the spectra except that of α-Sb_2O_4 are single, quadrupole-split
peaks. Values for the isomer shifts and other experimental parameters are
reported in Table II. Quadrupole splitting (Q.S.) has been reported from NQR
measurements for both cubic (10) and orthorhombic (11) Sb_2O_3 as 554.83 and
541.4 MHz, respectively. Our values are 548 $\pm$ 12 MHz for cubic Sb_2O_3 and
509 $\pm$ 15 MHz for orthorhombic Sb_2O_3. The Q.S. values obtained by NQR are
several orders of magnitude more precise than the Mössbauer results. However,

the quadrupole splitting cannot be ignored in analysis of the [121]Sb spectra,
and NQR results are not always available. The asymmetry parameter, η, affects
the shape of the curve to an observable extent only if greater than ~0.3 (11).

TABLE II

Experimental Values of the Mössbauer Parameters

| Compound	I.S. relative to [121]SnO$_2$(Sb) (mm/sec)	Q.S. (mm/sec)	W full width at half maximum (mm/sec)
Sb$_2$O$_3$, Baker Reagent	−11.38 ± 0.10	18.6 ± 0.7	3.20 ± 0.15
Sb$_2$O$_3$, Cubic	−11.32 ± 0.12	18.3 ± 0.4	3.14 ± 0.10
Sb$_2$O$_3$, Orthorhombic	−11.33 ± 0.07	17.0 ± 0.2	2.89 ± 0.11
Sb$_2$O$_3$, Amorphous	−11.35 ± 0.10	18.6 ± 1.0	3.60 ± 0.21
α−Sb$_2$O$_4$	+ 0.61 ± 0.03	−6.1 ± 1.0	3.31 ± 0.15
	−14.36 ± 0.06	16.4 ± 0.6	3.13 ± 0.14
Sb$_2$O$_5$	+ 1.06 ± 0.02	−4.3 ± 1.1	3.49 ± 0.13

The only oxide having η large enough to observe was orthorhombic Sb$_2$O$_3$, for
which a better computer fit was obtained when η was allowed to vary. The
result is η = 0.51 ± 0.14 (this compares to 0.36 from NQR (12)).

The spectrum of α−Sb$_2$O$_4$ shows two widely spaced peaks (Fig. 1) of equal
area which have isomer shifts characteristic of Sb(III) and Sb(V). This
spectrum provides direct confirmation of the conclusion reached by Skapski and
Rogers (5) from their x-ray studies that this compound contains antimony in
two oxidation states (Sb(III, Sb(V) rather than Sb(IV)).

The isomer shift values for the various Sb$_2$O$_3$ samples (Table II) are
identical. This is, at first, somewhat surprising since there are two dis-
tinct allotropic modifications represented: the cubic form which consists of
discrete Sb$_4$O$_6$ molecules (13) and the orthorhombic form which consists of
infinite chains (14). In each case, however, there are three nearest

neighbor oxygen atoms for each antimony at a distance of 2.0 A, and even though

the bond angles differ slightly, the geometric arrangement about the antimony

is very similar in both cases. It is also gratifying to note the arrangement

in isomer shifts determined independently by three different groups for both

Sb_2O_3 (11.1 $\pm$ 0.3) and Sb_2O_5 (0.8 $\pm$ 0.5) (*cf*. Tables I and II).

FIG. 1. ^{121}Sb Mössbauer Spectrum of $\alpha-Sb_2O_4$

Velocity (mm/sec)
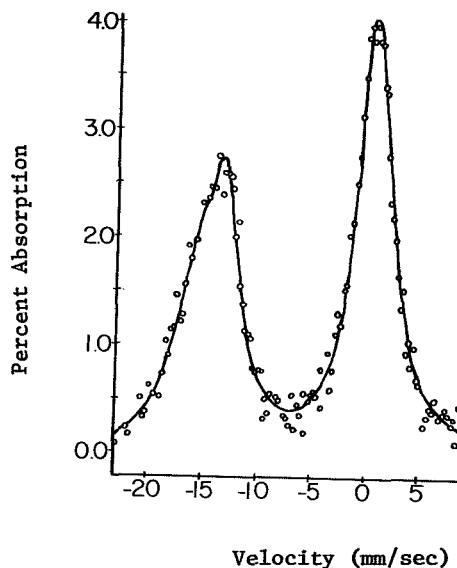
The isomer shift of -14.36 mm/sec for Sb(III) in $\alpha-Sb_2O_4$ is quite

different from that found in Sb_2O_3 (-11.32 mm/sec), presumably due to a

change in the coordination about the antimony. Indeed, it has been shown

that in $\beta-Sb_2O_4$ the Sb(III) has two oxygen neighbors at 2.032 A forming a

90° bond angle with the antimony and two additional oxygen neighbors at 2.218 A

forming a 150° bond angle with the antimony (6). The more negative isomer

shift of the Sb(III) in $\alpha-Sb_2O_4$ is indicative of an increase in *s* electron

density at the antimony nucleus as compared with that in Sb_2O_3. Assuming that

the bond distances and geometries about the Sb(III) are similar in both Sb_2O_4

allotrophs, the more negative value of the isomer shift of the Sb(III) in

$\alpha-Sb_2O_4$ might be rationalized either as due to the formation of fourth bond

with an oxygen atom electron pair, or due to less withdrawal of electrons by the two oxygens at 2.0 A as compared with three oxygens in Sb_2O_3.

The isomer shift and the quadrupole splitting values for the Sb(V) in α-Sb_2O_4 and in Sb_2O_5 are very similar, and one might anticipate that the bonding and geometry about the Sb(V) in these compounds is similar.

Acknowledgements

References

1. RUBY, S. L., KALVIUS, G. M., SNYDER, R. E., and BEARD, G. B., *Phys. Rev.*, 148, 176 (1966).

2. RUBY, S. L., KALVIUS, G. M., BEARD, G. B. and SNYDER, R. E., *Phys. Rev.*, 159, 239 (1967).

3. RUBY, S. L. in GRUVERMAN, I. J., ed., "Mössbauer Effect Methodology," Vol. 3, p. 203, Plenum Press, New York (1965).

4. BRUKHANOV, V. A., IOFA, B. Z., KOTKHEKAR, V., SEMENOV, S. I. and SHPINEL, V. S., *Soviet Phys. JETP Eng. Transl.*, 26, 912 (1968).

5. SKAPSKI, A. C. and ROGERS, D., *Chem. Commun.*, 1965, 611.

6. ROGERS, D. and SKAPSKI, A. C., *Proc. Chem. Soc.*, 1964, 400.

7. ROBERTS, E. J. and FENWICK, F., *J. Amer. Chem. Soc.*, 50, 2125 (1928).

8. SWANSON, H. E., COOK, M. I., EVANS, E. H. and deGROOT, J. H., *Nat. Bur. Stand. U. S. Circ.* 539, 10, 6 (1960).

9. SWANSON, H. E., FUYAT, R. K. and UGRINIC, G. M., *Nat. Bur. Stand. U.S. Circ.* 539, 3, 31 (1954).

10. BARNES, R. G. and BRAY, P. J., *J. Chem. Phys.*, 23, 1177 (1955).

11. STEVENS, J. G. and BOWEN, L. H., in GRUVERMAN, I. J., ed.,"Mössbauer Effect Methodology," Vol. 3, p. 000, Plenum Press, New York (1969).

12. SAFIN, I. A., *J. Struct. Chem. USSR Eng. Transl.*, 4, 242 (1963).

13. ALMIN, K. E. and WESTGREN, A., *Arkiv Kemi*, 15B, 22 (1942).

14. BUERGER, M. J. and HENDRICKS, S. B., *Z. Krist.*, 98, 1 (1938).